2006 ERSD Annual Report
Project #90258

Microbial Transformations of TRU and Mixed Wastes: Actinide Speciation and Waste Volume Reduction

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Results To Date

Recent results associated with Objective I:

During the past year, both a graduate student and a visiting summer undergraduate research assistant have conducted experiments concerning interaction of metals with fresh and aged cellulosic materials. Molybdenum and tungsten compounds were chosen for a number of reasons.

1. As analogs for transuranics:

In order to test experimental techniques, including complementary electrochemistry and vibrational spectroscopy, it is necessary to use approximate chemical analogs (non-radioactive) for transuranic materials (including Np, Pu, Am and Cm). Analogs need to compare as closely as possible in several regards:

i. Periodic table similarity ii. Ability to exist in multiple oxidation states iii. Similarities in terms of core electronic structure iv. Formation of similar compounds with oxygen and hydroxyl v. Similar potential-pH behavior vi. Reactivity with organic ligands

While no analogs will be perfect in this regard, matching as many as possible of these criteria is desirable. For example, W has been used as a homolog for U. Using the criteria stated above, there are some distinct similarities:

i. W is a group VIA element ii. W exists in 6, 5, 4 and 3 oxidation states (though it also exists, rarely, in a divalent state) iii. W tends to form hexavalent compounds at neutral pH or higher, with two doubly bonded oxygens iv. Some similarity in E-pH diagram, especially in oxidizing environment (and high pH) v. Remains in soluble state at high pH

Differences include:

i. Tendency to form tungstate oxyanion as opposed to dioxournaium cation under some conditions ii. Differences in E-pH diagram, especially at low pH iii. Despite having an f-

orbital structure (as in actinides), doubly bonded oxygen forms a “bent” (122 degree) structure (unlike axial dioxouranium).

Despite these differences, and since U(IV) has also been used as an analog for Pu(IV) compounds, W was used in vibrational spectroscopic studies involving fresh and aged cellulosic materials. Mo has also been used for several reasons:

i. Group VIA element ii. Tends to form multiple oxidation states (6,5,4,3, and, rarely, 2) iii. Two doubly bonded oxygens at high pH, oxidizing environment (though also having a “bent” structure). iv. Mo(VI) in dioxo forms analogous organically liganded structures v. Formation of multiple solid phases at near neutral pH and open circuit conditions has also been noted (similar to U, Pu and Np). vi. A great deal of data available on spectroscopy of Mo for comparison.

Molecular modeling using these analogs has also been more straightforward. The data thus obtained may be used for comparison to models of transuranics.

While both W and Mo form oxyanions (tungstate and molybdate, respectively) which are soluble, it has been shown that structures including molybdic acid or tungstic acid may form which may show some structural similarities to uranyl hydroxide. In addition, all three complexes are oxidizing agents for surfaces to which they are exposed (earlier work showed uranyl acceleration of iron oxidation). However, it would be instructive to expose materials to possible molybdenyl or tungstyl ions. These would be similar to uranyl, neptunyl or plutyl in that they would form cations due to the unpaired d-electron.

2. As a component of mixed waste

In addition, both Mo and W are components of stainless steel alloys often used in actinide processing facilities or as part of hazard waste containers, including hastelloy C-22 in which Mo and W are critical to the corrosion resistance of the container. This alloy will be used in the outer container for the Yucca Mountain facility, while 316 stainless steel (which also contains Mo) will be used for the inner container. This would lead to their inclusion in mixed waste products with transuranics, especially as stored/disposed stainless steel materials and containers react with their environment, either through purely chemical redox reactions or due to the presence of sulfate reducing bacteria (SRB). This category of anaerobic microbes can reduce the molybdates and tungstates oxyanions which are part of the corrosion protective (passive) layers on normally corrosion-resistant alloys (as we have shown in previous work). This would lead to release of these materials into the environment, following microbial degradation of alloys stored with mixed waste or which are part of the waste container composition.

Exposure of both fresh and aged cellulosic samples to molybdate/deuterated water and tungstate/deuterated water solutions indicated complexation at the hydroxyl and glycosidic ligands. This was analyzed through a combination of FTIR and Raman

microspectroscopic mapping, scanning electron microscopy (SEM) and energy dispersive X-ray analysis. Samples were exposed both at a high pH (12) (to simulate WIPP repository conditions), and at lower pH (8.5-10.5). Samples were also exposed to low (0.1M) and high (1M) concentrations of molybdate and tungstate. SEM shows a broad dispersion of nanocrystalline molybdates and tungstates, only a portion of which can be removed by subsequent rinsing. The broadness of peaks corresponding to metal oxyanions and to alcohol deformation is indicative of disorder, which resulted from changes in bond angles around glycosidic linkages and hydrogen bonds associated with metals complexes. These results are currently in preparation for a publication.

In addition to the activities summarized above, further work is currently being done in analyzing the structure of complexes formed between U and transuranics analogs with isosaccharinic acid. This work will also involve a new graduate student brought into the program this year.

Recent results associated with objective II:

Electrochemical analysis of analogs (U, W, Mo) complexed with organic ligands with in situ vibrational spectroscopy (in progress)

In the third year of the program, we will be continuing to analyze the redox reactions of organically complexed U and TRU analogs with varying pH in order to gain a clearer picture of the structural transformations which accompany electron transfer reactions. Such reactions will provide further insight into microbial activity, and provide important data for development and optimization of remediation technologies based on bio-organic complexes. In order to facilitate this work, a portable, high sensitivity potentiostat with associated physical electrochemistry software will be purchased form Gamry, Inc. This system will be used with the electrochemical cells developed for both the Raman dispersive and FTIR spectrometers, and will also be able to be transported to other facilities at Stony brook or Brookhaven National Laboratory for studies. A new graduate student joining the program in 2005 will be assigned to perform this analysis.

Recent results associated with objective III:

Structural analysis with vibrational and X-ray spectroscopy will be complemented by computational molecular modeling of the possible complexes using both Gaussian and Amersterdam Density Functional analysis (the latter based on Slater type orbitals and optimized for heavy metal complexes up to atomic number 106) on a new dual core processor computer at Stony Brook. The computer and software have been installed.

Particular attention will be paid to hydration numbers and solvation shells of ions and complexes. Such information has previously been calculated using Hartree-Fock methods and a hydration number of five was found to be most stable. Solvartion shells are currently being modeled in association with J. Kubicki of Penn State University; such information will be extremely valuable to not only improve accuracy of calculation

of vibrational frequencies for comparison with empirical results, but also to help explain kinetic effects and surface interactions which govern transport phenomena.

We have recently developed models for uranyl-oxalate complexes, uranium-catecholate structures, uranyl-malate structures, and uranyl-salicylate structures at varying pH. These are being further analyzed by a unique combination of molecular modeling (with J. Kubicki at Penn State) and NMR spectroscopy at Stony Brook. This work has been presented at a recent conference.

Deliverables:

1. Halada, Gary P.; Eng, Charlotte W.; Phillips, Brian L. Multi-disciplinary approach to integration of complementary spectroscopies and molecular modeling for analysis of uranium-organic complexes. Abstracts of Papers, 230th ACS National Meeting, Washington, DC, United States, Aug. 28-Sept. 1, 2005 (2005)

2. Vasko, Stephanie, E; Eng, Charlotte; Halada, Gary, “The Degradation, Complexation, and Chemistry Of Cellulose With Transuranic Analogues: A Study Of The Interaction Of Cellulose With Na2MoO4 2H2O AND Na2WO4 2H2O”, Sixteenth (16th) Annual Argonne Symposium For Undergraduates In Science, Engineering And Mathematics November 4-5, 2005, Argonne National Laboratory

3. Halada, Gary P.; Eng, Charlotte W.; Phillips, Brian L. Understanding the charge transfer-induced molecular transformation of uranium-organic complexes using molecular and synchrotron spectroscopies combined with electrochemistry. Abstracts of Papers, 229th ACS National Meeting, San Diego, CA, United States, March 13-17, 2005 (2005)

4. Halada, Gary P., “Complementary Spectroscopic Techniques to Model the Association of Contaminant Uranium with Structural Surfaces”, accepted for publication in Journal of Electron Spectroscopy and related Phenomena (2005)

5. In preparation (2), including “Complexation of Uranium by Organic Ligands: Implications for Bioreduction and Stability”, and “In Situ Electrochemistry/Fourier Transform Infrared Spectroscopy of Organic and Organometallic Molecules”, by G.P. Halada, C.W. Eng and K. Volgensky